Problem set 1 – Soft Matter

Problem 1

Due to gravity colloidal particles in suspension form of a sedimentation equilibrium, which is characterised by a height-dependent number density $n(z)$. The (osmotic) pressure at a height h (w.r.t the bottom of the container) at low concentrations (i.e. assuming no interactions) is given by $\Pi(h) = n(h)k_BT$.

a) Explain what is meant by the buoyant mass of a colloidal particle of mass density ρ_c in a solvent of mass density ρ_s? Write down the expression for the gravitational force acting an a particle in terms of the particle volume V and the mass density difference $\Delta\rho = \rho_c - \rho_s$.

b) The upward force, due to the osmotic pressure gradient, acting on a particle in a sedimentation equilibrium is given by

$$F_{up} = -\frac{1}{n(h)}\frac{d\Pi}{dh}.$$

Verify by dimensional analysis that this expression indeed has the units of a force.

c) Balance the forces from parts a) and b) and solve the resulting differential equation to obtain the so-called *barometric height distribution* for the particle density n as a function of height h:

$$n(h) = n(0)\exp\left(\frac{-\Delta\rho V g h}{k_BT}\right).$$

d) Calculate the decay length – which is often referred to as the *gravitational length* – of the exponential function (i.e. the height at which $n(h)/n(0) = e^{-1}$) for polystyrene particles of diameter

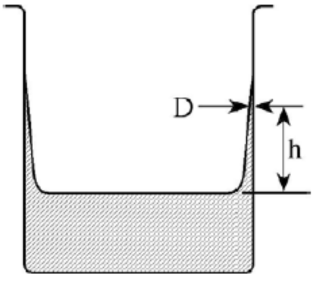
- 0.1 μm
- 1 μm
- 10 μm

in water at 300 K. Note that the density of polystyrene = 1.05 g cm^{-3}.

Comment on the values you obtain, especially in relation to the extent of the Earth's atmosphere (what would be the gravitational length of an oxygen molecule?).

Problem 2

When octane is placed in a quartz vessel, the octane wets the walls of the vessel as schematically shown in the figure below.



The energy, U, per unit area of a film of octane of thickness, D, due to van der Waals interactions can be described by

$$U(D) = \frac{-A}{12\pi D^2},$$

where the Hamaker constant $A = -7 \cdot 10^{-21}$ J.
The gravitational potential energy per unit area of the film at a height, h, above the liquid surface is given by $U = \rho g h D$, with ρ the density of the liquid (= 703 kg m^{-3} for octane) and $g = 9.81$ m s^{-2}.

a) Sketch the form of each of these two potentials (for $A < 0$), and of their sum, as a function of D.

b) Evaluate the equilibrium thickness of the film at $h = 1$ cm.

The Hamaker constant for water interacting with itself across a vacuum is $A_{ww} = 3.7 \cdot 10^{-20}$ J while for a typical hydrocarbon oil, $A_{oo} = 5.1 \cdot 10^{-20}$ J.

c) Estimate the Hamaker constant, A_{wo}, for water interacting with oil across a vacuum.

d) Determine the sign of the Hamaker constant for a film of oil on water in air. Note that the combining relation for medium 1 interacting with medium 2 across medium 3: $A_{132} \approx A_{12} + A_{33} - A_{13} - A_{23}$.

e) Hence predict whether oil will spread on water.

Problem 3

The Debye length depends on the salt concentration via the bulk number density n_0 as given by

$$\kappa^{-1} = \sqrt{\frac{\epsilon\epsilon_0 k_B T}{2e^2 n_0 z^2}},$$

where ϵ is relative permittivity, ϵ_0 the permittivity in vacuum ($\epsilon_0 = 8.85 \cdot 10^{-12}$ C^2/N m^2), z the valency of the ions and e the elementary charge.

a) Calculate the Debye length in 1.00 mM KNO_3 (for water at $T = 298$ K and $\epsilon = 78$).

b) Explain whether the Debye length will be smaller or larger in a solution of (i) 1.75 mM KNO_3 and (ii) 1.00 mM K_2SO_4?

The exact solution of the Poisson-Boltzmann equation for a charged surface is given by the Gouy-Chapman equation for the dimensionless electrostatic potential:

$$\Phi(x) = 2\ln\left[\frac{1 + \tanh(\Phi_0/4)e^{-\kappa x}}{1 - \tanh(\Phi_0/4)e^{-\kappa x}}\right].$$

c) Show that for small dimensionless surface potentials, i.e. $\Phi_0 \ll 1$, the solution to the linearised Poisson-Boltzmann equation is recovered ($\Phi(x) = \Phi_0 e^{-\kappa x}$).

Hint: Use that for $x \ll 1$ $\tanh x \approx x$ and $\ln(1 + x) \approx x$ (also in that order actually!)

d) Explain what is meant by the electric double layer and what the significance of the Debye length κ^{-1} is in this respect?

The relation between the thickness of the double layer and κ^{-1} can also be demonstrated using the condition for electro-neutrality. The surface charge density (of the charged surface), σ, must be exactly matched by the integrated charge density in the solution, $\rho(x)$:

$$\sigma = -\int_0^\infty \rho(x)dx.$$

e) Given that for small surface potentials, $\rho(x) \approx -2zen_0\Phi(x)$, show that

$$\sigma = \epsilon\epsilon_0\kappa\phi_0.$$

Note that this result is identical to that for a dielectric-filled capacitor with charge σ, potential ϕ_0 and a plate–plate separation of κ^{-1}; hence the analogy between the thickness of the electrical double layer and the separation between the oppositely charged plates of the capacitor.

f) Calculate ϕ_0 for a typical surface charge density of colloids in water, $\sigma = 1$ e/nm^2, and a salt concentration of 0.1 M NaCl. Is the linear Poisson-Boltzmann equation, valid for $\phi_0 < 26$ mV, typically applicable for colloidal particles?

Problem 4

a) The Van der Waals interaction between two spheres of radius R and separated by a distance D is given by $U = -AR/12D$, where A is the Hamaker constant.

   - Calculate U between two $R = 0.5\ \mu\mathrm{m}$ silica spheres ($A_{11} = 6 \cdot 10^{-20}$ J) separated by 100 nm in vacuum.
   - Repeat the calculation for silica in water, where $A_{131} = 0.8 \cdot 10^{-20}$ J.
   - Compare both values to the thermal energy of the particles at room temperature.

In the lectures, the Van der Waals interaction (per unit area) between two half spaces was calculated. Here, we will follow the same strategy to calculate the Van der Waals interaction (per unit area) between two plates of finite thickness T at a separation D, as shown in the diagram below.

b) Starting from the interaction between two atoms being $U = -C/r^6$, first show that the interaction between 1 atom and a plate of thickness T and number density ρ, separated by a distance D, is

$$U(D) = -\frac{\pi C\rho}{6}\left(\frac{1}{D^3} - \frac{1}{(D+T)^3}\right).$$

Hint: use that $xdx = \frac{1}{2}dx^2$.

Note that for $T \to \infty$ the 'atom – half space' interaction is recovered $(-\pi C\rho/6D^3)$.

c) Next, calculate the interaction between two plates by integrating over the second plate of thickness T and number density ρ and express your answer in terms of the Hamaker constant $A = \pi^2 C\rho^2$. Hence, show that the Van der Waals interaction (per unit area) between two plates of thickness T at a separation D is

$$U(D) = -\frac{A}{12\pi}\left(\frac{1}{D^2} - \frac{2}{(D+T)^2} + \frac{1}{(D+2T)^2}\right),$$

Note again that for $T \to \infty$ the 'half space – half space' interaction is recovered $(-A/12\pi D^2)$.